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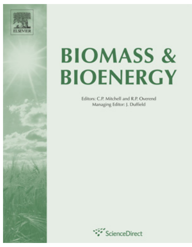

Cascaded production of biogas and hydrochar from wheat straw: Energetic potential and recovery of carbon and plant nutrients

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ABSTRACT

The increasing interest in biogas production has brought notable attention to lignocellulosic wastes as a promising and yet unexploited feedstock. As these materials are usually highly recalcitrant the energetic efficiency of biogas production, however, is comparatively low. With the aim to overcome this drawback, a novel cascaded approach was investigated that combines anaerobic digestion with hydrothermal carbonization (HTC). The latter is used to convert the digestate into a carbon-rich product termed hydrochar. An energetic evaluation of this cascaded treatment shows that the energy recovery can be nearly doubled compared to single anaerobic digestion.

Furthermore, systematic HTC experiments with both fresh and digested wheat straw and with reaction temperatures of 190 °C, 210 °C, 230 °C, and 250 °C revealed an effect of reaction temperature on carbon, nitrogen, and phosphorus concentration in the final hydrochar. Carbon, nitrogen and phosphorus are primarily retained in the hydrochar, which could favor its use as soil ameliorant instead of an energy carrier.

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1. Introduction

The use of anaerobic digestion for the energetic use of agricultural waste is increasing rapidly. In most cases the digestate is returned to the field as organic fertilizer. However, depending on the size of the biogas plant and transportation costs field application of digestate is not always economically feasible. Additionally, the amount of digestate that can be applied is limited due to its relatively high ammonia content and digestate can account for a significant release of green house gases especially N_2O, NH_3, and CH_4. This issue has been recognized by research institutions and various potential solutions are investigated such as composting, drying, and pelleting [1–3].

A newly discovered possibility to treat digestate and create a value-added product is the thermochemical conversion into a carbon and energy rich product, which can be used as a high-quality alternative fuel or as a soil amender and carbon sink. Both pyrolysis, used by mankind since ancient times [4], and hydrothermal carbonization (HTC) can be used for this purpose. In comparison with HTC, pyrolysis requires dry feedstock and therefore the digestate needs to be dried prior to carbonization. Considering the total solids content of typical digestate, usually 2–10% of fresh matter [1], drying requires a substantial amount of energy. Therefore, the application of the wet conversion process HTC seems to be beneficial.

HTC is a thermochemical conversion process which has been used to simulate natural coalification for decades [5,6].

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Abbreviations

daf	dry, ash-free
DM	dry matter
HTC	hydrothermal carbonization
ODM	organic dry matter
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
UASS	upflow anaerobic solid state

Reactions are carried out in a pressure vessel, containing biomass submerged in liquid, with temperatures of 180–270 °C [7]. Pressures of the reaction are not controlled and are slightly above the saturated vapor pressure due to gaseous by-products [8]. HTC has been applied for a variety of feedstock [9–14]. The main product is solid material with a similar energy density as lignite.

Caused by a partial destruction of the biomass structure by the HTC process, the char product shows an improved dewatering ability, which enables mechanical separation [14,15]. Thus, HTC could be regarded both a conversion process to increase the energy density and dewatering ability of wet biomass resulting in a product with increased value as a fuel [8,9,11,12,16]. Despite the energetic advantage of a mechanical dewatering, model calculations showed different results for the liability of HTC in conversion chains depending on the scenario chosen [17,18].

The aim of this investigation is to determine the benefits gained by carbonizing the digestate from anaerobic digestion by HTC. The focus is placed on the fate of plant nutrients during anaerobic digestion and carbonization and on evaluating the cascaded process in respect to its energetic potential and the carbon and nutrient recovery.

2. Materials and methods

2.1. *Anaerobic digestion*

Anaerobic digestion of the wheat straw was carried out using the upflow anaerobic solid-state (UASS) process with process liquor circulation [19]. The wheat straw was obtained from winter wheat (*Triticum aestivum* L.) harvested in July 2009 by Dittmannsdorfer Milch GmbH in Kitzscher (Germany) (N 51° 8′ 48″, E 12° 32′ 26″). Before its use, the straw was recovered from the field as long baled straw, shred in two stages to a target chopping length below 20 mm, dedusted by a cyclone, compressed into 20–25 kg plastic-wrapped quad bales, and stored in this state for about one year under dry conditions. Each bale was sampled separately by taking and mixing material from various random locations of the bale (analyses are shown in Table 1). A pair of identical 40 L UASS reactors was operated for 200 days under thermophilic conditions (55 °C) at a fixed organic load rate (dry basis) of 2.5 g L^{-1}d^{-1} with wheat straw as the sole substrate. For the methanization of soluble metabolites, each UASS reactor was connected to an individual 30 L fixed bed reactor. In order to compensate the straw's lack of nutrients and water, nitrogen, trace elements, and tap water were added during reactor operation. The UASS reactors were fed five to seven days a week and the removal of digestate was carried out once a week. Process liquor was removed once a week for analytical purposes. A detailed description of the process performance has been published elsewhere [20].

2.2. *Hydrothermal carbonization*

The feedstock for the carbonization experiments was fresh wheat straw and digested wheat straw derived from thermophilic digestion as described above. For reference experiments, poplar wood, lignin, and microcrystalline cellulose were also carbonized. Japanese poplar was obtained from an

Table 1 – Composition of the feedstock expressed as mass fraction.

Composition (expressed as mass fraction)		UASS[a]	Hydrothermal carbonization[b]		
		Straw	Straw	Digestate	Poplar
ODM, db	(%)	94.8	95.1	94.4	99.0
Hemicellulose, db	(%)	n.a.	27.8	18.9	12.2
Cellulose, db	(%)	n.a.	45.8	44.6	60.9
Lignin, db	(%)	n.a.	8.5	21.4	19.0
Carbon, daf	(%)	48.4	49.4	51.2	51.1
Nitrogen, daf	(%)	0.4	0.8	1.2	0.3
Sulfur, daf	(%)	0.14	0.31	0.25	0.05
Hydrogen, daf	(%)	7.7	7.2	7.3	7.0
Oxygen, daf, by difference	(%)	43.3	42.3	40.1	43.7
TKN, db	(mg kg^{-1})	3800	7000	11,300	2700
Phosphor, db	(mg kg^{-1})	460	640	870	420
Potassium, db	(mg kg^{-1})	12,300	n.a.	8800	n.a.

daf: dry ash free basis.
db: dry basis.
n.a.: not analyzed.
a $n = 4$ samples.
b $n = 1$ sample.

experimental field at the Leibniz Institute for Agricultural Engineering in Potsdam, Germany, originally started in 1994 [21]. Kraft lignin (lignin, alkali CAS 8068-05-1) and hemicellulose (D-(+)-Xylose CAS 58-86-6) were obtained from Sigma Aldrich. Despite the advantage of HTC to allow for wet feedstock, the digestate was dried in an oven for three days at 60 °C to ensure a homogenous dry matter content and consistent carbon content. The results of the ultimate analysis of the feedstock are given in Table 1. Both materials were milled in a Retsch SM100 Cutting Mill with a 4 mm screen prior to carbonization [12].

The materials were weighed in a beaker, 35.81 g of straw or 33.52 g of digestate, and transferred to the 1 L reactor vessel. The same beaker was used to measure 580 g distilled water, which was then added to the vessel. These parameters were chosen to allow for the same carbon content in the reaction mixture of 26.6 g L^{-1} for every experiment while stirring of the suspension was still possible. However, the mass fraction of dry biomass in the reaction mixture was different for the feedstocks; 0.06 for straw and 0.05 for digestate.

A Parr 1-L, 4520 Series, stirred reactor was used for the experiments. A heating rate of approximately 3 K min^{-1} was observed, but was not controlled. The contents were continually stirred at 1.5 Hz. The reaction time was defined as the time maintained at the desired temperature, not including heating and cooling phases. A fractional factorial experimental design using temperature (190 °C, 210 °C, 230 °C, 250 °C) and feed as parameters was implemented. Additional experiments were conducted at 250 °C with reaction times of 1 h, 2.5 h, and 4 h. The material abbreviations are ST for wheat straw and D for digestate and the individual production runs were denoted as Material Abbreviation-Reaction Temperature-Reaction Time, e.g. ST-250-6. For each material, one replication was conducted at 230 °C for 6 h (ST-230-6-2 and D-230-6-2).

After the reaction time ended, the heating band was removed from the reactor. The stirrer was left running and the reactor remained closed until the internal temperature reached room temperature (~25 °C) and the residual pressure was around 0.02 MPa. The vessel was removed and the contents were filtered through folded paper (ROTH Type 113P filter) for 20 min. The fluid was collected, and then the hydrochar was rinsed with 160 mL distilled water and filtered for an additional 20 min. The filter and the hydrochar were placed in a glass petri dish and dried for 48 h at 60 °C.

2.3. *Analytical methods*

During the anaerobic digestion experiment the volumetric gas production of each reactor was measured with an individual TG05 multi-chamber rotor gas meter (Ritter, Germany). The gas produced in each reactor was separately collected in gas bags and periodically analyzed for CH_4, CO_2, O_2, and H_2S using an industrial biogas analyzer (SSM6000 from Pronova, Germany).

Elemental analysis (CHNS) was conducted with a Vario EL elemental analyzer; each sample was analyzed three times. Dry matter (105 °C) and organic dry matter (ODM) (550 °C) were determined according to VDLUFA Chapter 3.5 and 8.4 [22]. Ash content was calculated as Ash = 100−ODM. The elemental, ash and dry matter content of feedstock and hydrochar is always expressed as mass fraction in the following.

Total organic carbon (TOC) of the liquid phase was measured using a TOC Analyzer 5050A (Shimadzu Scientific Instruments, Columbia, MD, USA) and the method for measuring the non-purgeable organic carbon. Samples were measured until the standard error was <2%.

Total Kjeldahl nitrogen (TKN) and phosphorus (P) concentrations were determined by Kjeldahl digestion methods.

Liquid phase pH was measured directly after filtration using a WTW inoLab pH/Cond 720. For the measurement of biochar pH, as much dried char was added to distilled water to reach a dry mass fraction of 0.01 in the resulting mixture. The sample/water mixture was shaken for 15 min before measuring the pH.

Fiber analysis of the biomass has been conducted according to VDLUFA [22]. The lignin content has been determined via the acid detergent lignin fraction (ADL).

2.4. *Mass and energy balances*

The balances for the anaerobic digestion have been determined for ten weeks of steady state operation. During that period, the two reactors were fed daily and digestate was extracted once a week. Thus, balances have been determined once a week.

Mass balances have been set up on the basis of dry matter content (see above) and considered the solid fraction, the extraction of process liquor for analytical purposes as well as an accumulation in the reactor. The energetic content of the biomass and digestate was estimated using an empirical correlation [23] for the prediction of the heating value of biomass from its elemental composition. The accuracy of this prediction is around ±2% for a broad range of biomass [23]. The energetic content of the biogas has been calculated considering only its methane fraction, using a higher heating value of $HHV_{methane} = 890.7$ kJ mol^{-1} [24].

The balances for the HTC of straw and digestate have been determined batch-wise. The energetic content of the produced hydrochar has been estimated using a unified correlation for the prediction of heating values for a wide variety of fuels with an estimated accuracy of ±1.45% [25].

The balance of the cascaded process has been based upon the overall balance of ten weeks of operation of two UASS reactors and the results from HTC at 250 °C for 6 h (D-250-6).

3. Results and discussion

3.1. *Formation and characteristics of the digestate*

The analysis of the anaerobic digestion process revealed a methane yield of 0.165 L g^{-1} on the basis of the ODM input. This can be considered within the range of expectation when compared with results from other groups [26–28]. Solid digestate was removed once a week in a quantity of 3–4 kg fresh matter. The chemical characteristics of the removed digestate at steady state conditions are summarized in Table 2. The amount and composition of the ODM of the digestate was stable and showed no significant differences between the

Table 2 – Mass flows of two continuously operated UASS biogas reactors during steady state conditions over a timeframe of 68 days and composition of the digestate expressed as mass fraction. All values represent the means of weekly analyses.

		Reactor#1	Reactor#2
Biomass input dry basis	(kg d^{-1})	1.043 (0.001)[a]	1.043 (0.001)[a]
Methane yield	(kg d^{-1})	0.117 (0.003)[a]	0.121 (0.003)[a]
Digestate yield dry basis	(kg d^{-1})	0.67 (0.03)[b]	0.64 (0.04)[b]
Digestate composition			
DM	(%)	14.9 (0.59)[b]	14.3 (0.82)[b]
Carbon, daf	(%)	50.2 (0.74)[b]	50.2 (0.56)[b]
Hydrogen, daf	(%)	7.1 (0.33)[b]	7.1 (0.27)[b]
Nitrogen, daf	(%)	0.74 (0.07)[b]	0.73 (0.07)[b]
ODM, db	(%)	94.8 (0.4)[b]	94.8 (0.32)[b]
Phosphor, db	(mg kg^{-1})	800 (220)[b]	800 (280)[b]
Potassium, db	(mg kg^{-1})	7900 (810)[b]	7300 (620)[b]

daf: dry ash free basis.
db: dry basis.
a Standard deviation given by manufacturers of measurement equipment.
b Standard deviation estimated from ten samples.

two reactors. However, the content of nitrogen, phosphorus and potassium changed in both the digestate and the process liquor during the continuous operation (see Supplemental Figs. S1 and S2). In the case of nitrogen this is clearly due to the increased addition of nitrogen in form of ammonium carbonate, which represented 80% of the total nitrogen input into the system. Based on these observations it has to be concluded that the reactor system was not a chemostat and therefore not in a true steady state despite a stable biogas production [20].

More surprisingly, the elemental balances of nitrogen, phosphorus, and potassium could not be closed satisfactorily even when considering the accumulation in the process liquor (see Supplemental Fig. S3). Ammonia is lost during drying of the digestate prior to its analysis, which explains the apparent sink in this elemental balance. However, this cannot explain the behavior of phosphorus and potassium. While the balance for phosphorus is closed in sum for the operation of ten weeks, there is a sudden source for phosphorus of 55–70% of the input material in the last two weeks (60–90% in the second reactor). This corresponds to its depletion in the process liquor, however, the reason for this sudden release of phosphorus is not known. Potassium exhibits no specific trend but is characterized by losses of 30% during ten weeks of operation (45% in the second reactor). In conclusion, calculated NPK recovery rates in the digestate (without respecting process liquor accumulation) were 21% of nitrogen, 111% of phosphorus, and 41% of potassium for a period of 10 weeks of continuous operation (20% of nitrogen, 109% of phosphorus, and 36% of potassium for the second reactor). These observations are interesting, because anaerobic digestion is usually considered to preserve almost all plant nutrients [29]. The loss in potassium cannot be properly explained by an accumulation in the process liquor. Further investigations are required to explain these phenomena.

The balance for carbon could be closed satisfactorily, 66% of carbon were recovered in the digestate (63% for the second reactor) and the rest in the biogas. For the case of carbon, the observed accumulation in the process liquor (see Supplemental Fig. S2) has minor effects on the overall balance.

3.2. *Formation and characteristics of the hydrochar*

Char yield exhibited a dependence on feedstock with digestate yielding from 37% at 250 °C, 6 h to 66% at 190 °C, 6 h (see Fig. 1). In comparison, char yield for straw was between 33 and 57%. The values for digestate agree with results from previous work with corn silage digestate in which char yields ranged from 35 to 71% [30]. However, Wirth et al. [31] report even lower straw mass yields of 39–49%, and Ramke et al. [14] considerably higher digestate-based char yields; most likely due to different HTC process parameters and material handling.

It can be hypothesized that the lower yield for straw is due to its lower lignin content. Easily available carbohydrates are being digested during fermentation leaving a digestate with higher lignin content than the original biomass. Carbohydrates yield less hydrochar as compared to lignitic biomass components [7]. In contrast to this theory, a similar yield for poplar and straw was observed for most of the experiments. Poplar contains even more lignin than the straw digestate, 26% and 21%, respectively.

Therefore, the hypothesis that char yield is dependent upon lignin, hemicellulose, and cellulose fractions is not necessary false, but using results from these experiments, it is not possible to develop a model or regression to predict char yield simply based on lignin, hemicellulose, and cellulose fractions.

3.2.1. *Carbon*

As shown in Fig. 2, the carbon content of the hydrochar had no strong dependence on the input material and was similar for each substrate at each temperature, ranging from 54 to 56% at 190 °C up to 73–74% at 250 °C for straw and digestate, respectively (see Fig. 2a). In terms of the ash content, the value for the char is lower than that of the original material with a decrease of about 0.03 observed for both feedstocks. Changes in ash content at increasing temperatures varied only within the range of uncertainty. This effect is a notably different

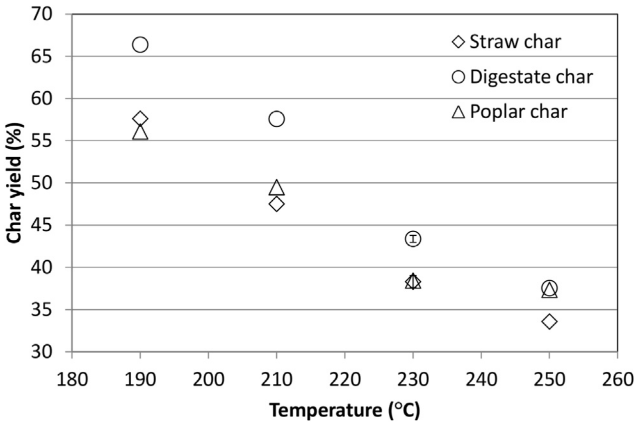

Fig. 1 – Char yield at different reaction temperatures.

characteristic than biochar in which ash content is higher than the original material after pyrolysis. Fuertes et al. [32] report an increase from 2.8 to 10.8% of ash content in pyrolyzed corn stover. Obviously, a significant fraction of the minerals is solved in the HTC process liquor. In contrast to this observation, individual elements can deviate from this trend as will be discussed below.

Carbon recovery rates in the hydrochar were highest for digestate and decreased with increasing temperature, with values ranging from 56 to 76% of the original carbon input. As shown in Fig. 3, overall 81–95% of the original carbon input was detected in the reaction products and the lowest rates were observed at higher temperatures and were generally lower for straw. Thus, the loss in carbon throughout the experimental procedure results in an uncertainty of the fate of carbon.

The amount of total organic carbon detected in the liquid phase is comparably high, i.e. up to 30% of the initial carbon of the straw or digestate [33]. This effect is a combination of the large volume of water compared to solid dry matter used for the experiments and the total organic carbon content of the process liquor, which is in the same order of magnitude as other reported results [15,18]. It is recognized that a dry mass fraction of more than 15% in the reaction mixture is favorable in order to run hydrothermal processes economically [34]. However, most hydrothermal experiments conducted report a dry mass fraction of 10% in the reaction mixture and even lower [35]. Based on these considerations, the significance of the presented results has to be limited for the specific experimental setup and procedure. Further research is required to investigate whether a substantially higher carbon recovery in the hydrochar can be achieved with a higher solids load and an optimized process design.

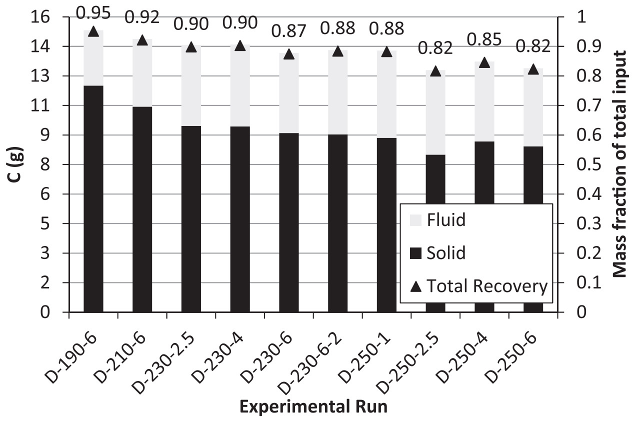

Fig. 3 – Carbon balances at different reaction conditions (carbonization of digestate; experimental runs are denoted as Feed-Temperature-Time (-Repetition)).

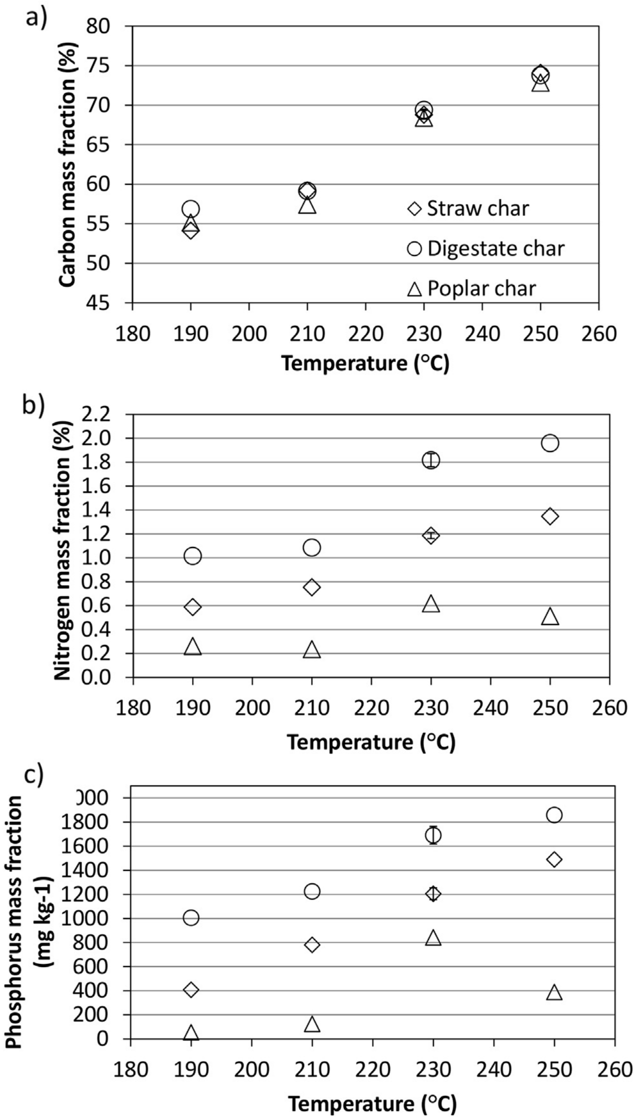

Fig. 2 – Carbon, nitrogen and phosphorus mass fraction in the hydrochar at different reaction temperatures. All values are given on a dry ash free basis.

The total organic carbon in the liquid phase represents a potentially problematic waste stream due to its high organic load which consists of a wide range of substances [9]. Although it is generally possible to reduce the organic load in the process liquor from HTC anaerobically [14,36], further research is required to better understand the potential risks and possible benefits associated with the process liquor before HTC can be put into practice.

3.2.2. *Nitrogen*

The nitrogen content of the produced hydrochars depends on the input material as well as the reaction temperature (see Fig. 2b). Notably, the nitrogen content of the hydrochar does not change significantly below 230 °C as compared to the initial content of the respective input material (see Table 1). The nitrogen content in the hydrochar almost doubles at 230 °C and 250 °C for all input materials. In contrast, the absolute nitrogen retention in the hydrochar is comparably stable at around 55–65% of the total nitrogen input for digestate (see Fig. 4). In straw samples, 48–64% of the original nitrogen input remained in the solid phase hydrochar. This observed nitrogen retention in the char is one aspect that differentiates hydrochar and biochar. In biochar, much of the nitrogen can be volatized during pyrolysis [37]. The observed nitrogen balances were closed comparably well to 97–108% for all experiments.

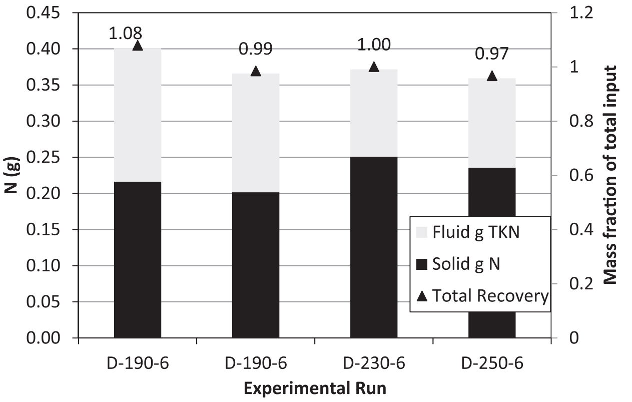

Fig. 4 – Nitrogen balances at different reaction conditions (carbonization of digestate; experimental runs are denoted as Feed-Temperature-Time).

3.2.3. *Phosphorus*

The phosphorus content of the produced hydrochars depends on the input material as well as the reaction temperature (see Fig. 2c). While the temperature dependency of the phosphorus content in the hydrochar appears to be qualitatively similar, there are some interesting differences between the substrates. The phosphorus content in the hydrochar from poplar was lower than in the original material for all reaction temperatures applied (the comparably high phosphorus content observed at 230 °C is treated as an outlier). In contrast, phosphorus content in the hydrochar product increased for all digestate samples, with final values ranging from 1005 to 2011 mg kg^{-1}. Compared to nitrogen, absolute phosphorus retention in the hydrochar was relatively high, ranging from 36 to 78% for the case of straw and 77–80% for the case of digestate (see Fig. 5). This observation contradicts results from Heilmann et al. [11] who reported complete loss of phosphorus from the solid material (corn distiller's grains) to the liquid phase after carbonization. However, it is noted that a reaction time of 2 h was used in these experiments. Also, a correlation between product pH and phosphorus retention in the hydrochar was observed in the experiments presented here. Reference experiments with poplar wood showed the lowest amount of phosphorus retention in the solid phase and, as seen in Table 3, the lowest initial and final pH values. These results support the suggestion made by Libra et al. [38] that the loss of phosphorus in the solid phase is due to the acidic nature of hydrochars and that this negatively affects its sorption capacity for phosphorus. However, the same authors also note that results are highly variable and other studies have also shown high retention of phosphorus. For example, Stemann and Ziegler [15] report that phosphorus largely remains in the solid phase in their experiments with poplar wood and leaves. Schneider et al. [39] reference a relatively low phosphorus concentration (6.4 mg L^{-1}) in the process fluid of biogas digestate char so it can be assumed that the retention in the solid phase is high. The phosphorus concentrations observed in these experiments are in the same order of magnitude as those reported by Schneider et al. [39] (5.44 mg L^{-1} for D-230-6 and 6.53 mg L^{-1} for D-250-6).

In contrast to the carbon and nitrogen balances in which the nutrients could be contained in the gas phase, phosphorus is found in the solid and liquid HTC products only. The balances for phosphorus were closed from 91 to 100% for all experiments.

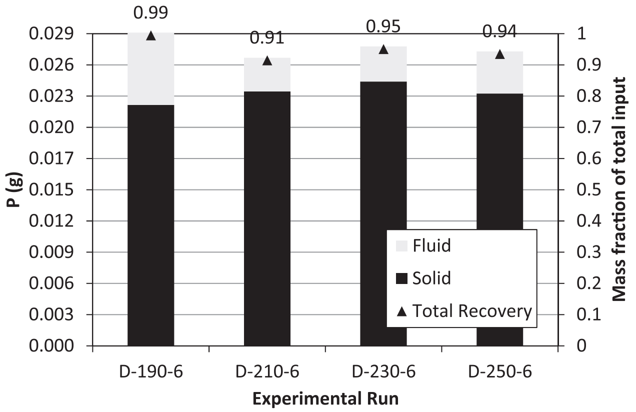

Fig. 5 – Phosphorus balances at different reaction conditions (carbonization of digestate; experimental runs are denoted as Feed-Temperature-Time).

3.2.4. *Potassium*

Unfeasibly high recovery rates of around 160% of the total input have been observed for the balance of potassium. This is primarily contributed to its concentration in the HTC process liquor. The retention of potassium in the hydrochar was around 1%. It is well known that potassium is primarily solved in the liquid phase under hydrothermal conditions [40], however, Stemann and Ziegler [15] reported a recovery of 12% in hydrochar (23% with process liquor recirculation). Further research is required to address this discrepancy.

3.3. *Balances of the cascaded biogas and biochar production*

Due to the recalcitrant nature of straw, two thirds of the carbon remain undigested under the applied conditions. By introducing the cascaded UASS-HTC process, the recovery of carbon by valuable products is more than doubled, which is directly reflected by a corresponding increase in the energetic efficiency (see below). At the same time, phosphorus is primarily retained in the solid product hydrochar (around 80% of the total input). Phosphorus represents a valuable resource with the second highest energy demand contributing to NPK fertilizer production [41]. The combustion of hydrochar leads to a withdrawal of this element from regionally closed nutrient cycles. Therefore, a regional use of the hydrochar as a

Table 3 – pH and acetic acid concentrations.

	Initial pH	Final pH[a] (fluid)	Final pH[a] (char)	Acetic Acid (g L^{-1})
Straw	7.92	3.89	4.56	2.79 (250 °C)
Digestate	9.08	4.2	4.73	1.85 (230 °C)
Poplar	6.73	3.62	4.16	2.34 (250 °C)

[a] Values are average of 4 reactions.

soil amendment should be taken into consideration [38]. Alternatively, the HTC process could be optimized in order to retain more phosphorus in the liquid phase. Changing the reaction temperature of HTC influences the phosphorus content in the hydrochar, however, the total hydrochar mass yield is affected at the same time. In consequence, reaction temperature has little effect on the distribution of phosphorus between liquid and solid phase products (see Fig. 5). It is indicated that the control of the process liquor pH and the residence time for HTC (as discussed above) is able to increase the phosphorus concentration in the liquid phase and thus allow for flexibility in designing the cascaded process according to specific needs. Further research is necessary to describe the underlying effects in more detail.

Little conclusions can be drawn for the elemental fate of nitrogen and potassium as a consequence of the significant unknown losses during straw digestion and, in the case of potassium, questionable results from the balance of the HTC process. All balances of the cascaded process have been included in the Supporting Information.

3.4. *Energetic potential*

For the case of the anaerobic digestion of straw, the digestate proves a significant waste stream which contains around 60% of the total energy input by the initial feed (see Fig. 6). The digestate has a similar higher heating value as the substrate. By means of HTC, around 50% of the digestate total energy input has been recovered in the hydrochar, The produced hydrochar represents a valuable fuel with an estimated higher heating value (on a DM basis) of 31.5 MJ kg^{-1}. As a result, 65% of the initial biomass energy can be recovered in the high value fuel products biogas and coal with this novel integrated process design. Thus, the energy recovered from straw can be nearly doubled by combining anaerobic fermentation with subsequent carbonization of the digestate (see Fig. 6).

The average energetic requirement to run the anaerobic digestion process can be considered 25% (heating and electricity) in respect to the produced gas [42]. This corresponds to 8% of the initial energy input by the substrate for the results of the UASS continuous operation. In contrast to anaerobic digestion, there are no reliable measurements of the energy required to run an HTC process and produce a dried hydrochar to date. However, there have been model calculations published which estimate this energetic requirement to roughly $<10\%$ of the energy contained in the product. This value includes the amount of energy required to dry the hydrochar to a water content $<10\%$ [17,43]. Considering these estimations of the auxiliary energy required to run the processes, the cascaded process has an energetic efficiency of 54% as compared to 26% of the single anaerobic digestion.

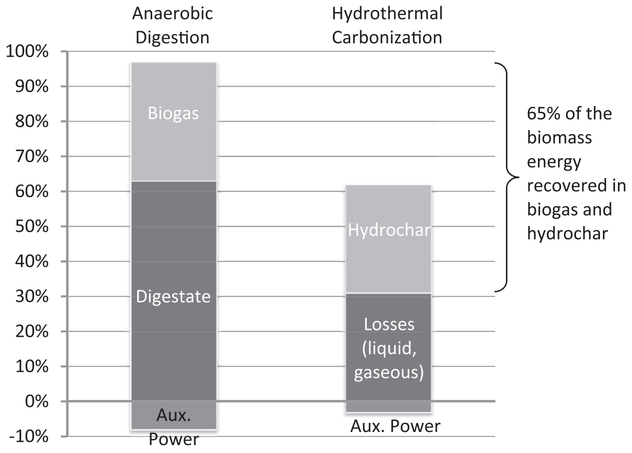

Fig. 6 – Energy balance of combined anaerobic fermentation and hydrothermal carbonization of wheat straw.

It is noted that the energy required to run the HTC process is highly dependent on the DM mass fraction in the feed. The values reported by Stemann and Ziegler [43] are for a DM content in the feed as low as 25%. Mechanical dewatering of the digestate would be a way to increase the efficiency of the carbonization process. Additionally, the referenced model calculations have been performed for stand-alone facilities of HTC. It is likely that the amount of external energy required to run the processes could be significantly reduced with an optimized, internal heat management in an integrated process of anaerobic digestion, a combined heat and power station and the HTC of the digestate. This internal heat management has to be addressed by further model calculations in order to prove the feasibility of this novel cascaded approach.

The results of the HTC of straw can be used to address the question of the feasibility of directly carbonizing straw instead of implementing a cascaded process. It has to be compared by which means the digestible part of the straw can be converted more efficiently. Naturally, the chemical energy from the digestible fraction is completely recovered as methane, minus 4% for microbial heat production [44]. Considering an auxiliary power of 25%, the digestible part of straw is converted to methane with an energetic efficiency of about 75%.

The results from the carbonization of straw showed that the energetic efficiency of its conversion is similar to that of digestate, i.e. the digestible part of straw is also converted with an energetic efficiency of 50%.

However, a higher conversion efficiency of HTC has been reported elsewhere [14,33] leading to a net energetic efficiency for the conversion process including auxiliary power of 70–80% [17,43]. Adding the higher value of methane as a fuel compared to coal and given its higher versatility in use, a combination of anaerobic digestion and carbonization might still be favorable, however, a final conclusion cannot be drawn from these first experiments.

It is noted that these results for the efficiency of a cascaded system are only valid for wheat straw and other lignocellulosic feedstock. The organic fraction of easier digestible biomass such as energy crops and the organic fraction of municipal solid waste can be reduced by 70–95% during anaerobic fermentation [1,45]. Consequently, the solid digestate represents a much lower waste stream and the benefit of an HTC integrated system regarding the overall energetic efficiency is reduced.

4. Conclusions

HTC was applied as a novel approach to upgrade the recalcitrant fraction of straw after anaerobic digestion to a valuable fuel ('hydrochar') with a higher heating value (on a DM basis) of 31.5 MJ kg^{-1}. For the case of anaerobic digestion of wheat straw it was shown by continuously operated UASS reactors that the digestate represents a significant residue with around 60% of the original energy introduced by the feedstock. More than half of that energy can be recovered in the produced hydrochar by hydrothermally carbonizing the wet digestate. Thus, the system integration of anaerobic digestion and subsequent HTC doubled the recovery of the energetic content of the straw as biogas and hydrochar to 65% and 54% considering auxiliary energy required to run the cascaded process.

Furthermore, an experimental design was conducted to analyze the distribution of elemental carbon, nitrogen and phosphorus in the liquid and solid phase products of the HTC process at four temperatures (190 °C, 210 °C, 230 °C, 250 °C) with a reaction time of 6 h for straw and straw digestate. Experimental replication showed a highly reproducible reaction with variations in carbon content of less than 1% and a maximum of 4% for nitrogen and phosphorus. In regards to the final product hydrochar, this work provides the first basis for understanding the distribution of the elements carbon, nitrogen, and phosphorus after the HTC of lignocellulosic materials. For the case of carbonizing digestate, the majority of nitrogen (60–65%) and phosphorus (77–80%) are recovered in the solid product hydrochar.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biombioe.2013.08.018.

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